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(54) 【発明の名称】 金属酸化物担持活性炭成型体

(57) 【要約】

【構成】炭素質原料を炭化し、水蒸気含有率15容量%以下の雰囲気中で賦活した後、そのままの雰囲気中で300℃以下まで冷却して得られた活性炭に、鉄、クロム、ニッケル、コバルト、マンガン、亜鉛、銅、マグネシウム及びカルシウムからなる群より選ばれた一種または二種以上の金属の酸化物を、0.1～20重量%を担持させた活性炭100重量部に、有機系バインダー1～50重量部を加えてハニカム状に成型せしめてなる、酸化触媒性を有する金属酸化物担持活性炭成型体及び、その成型体を使用することを特徴とする悪臭脱臭方法である。

【効果】本発明の金属酸化物担持活性炭成型体は常温あるいは低温で、かつ悪臭ガス濃度が極めて低い場合においても酸化触媒として高い機能を有し、またハニカム状のため圧損失が極めて低いためメチルメルカプタン、トリメチルアミン等悪臭物質の酸化除去能力に優れている。この特性を利用して冷蔵庫、トイレ、空気清浄機等のメチルメルカプタン等の悪臭ガスの除去剤に利用できる。

## PATENT ABSTRACTS OF JAPAN

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### (54) ACTIVATED CARBON MOLDED BODY CARRYING METAL OXIDE

#### (57)Abstract:

PROBLEM TO BE SOLVED: To obtain an activated carbon molded body having high function as an oxidation catalyst at ordinary temp. or low temp. even in the case of a very low concn. of malodorous gas by carrying a specified amt. of a metal oxide on activated carbon obtd. through specified processes, adding a binder and molding them in a honeycomb shape.

SOLUTION: Oxides of one or more kinds of metals selected from among Fe, Cr, Ni, Co, Mn, Zn, Cu, Mg and Ca are carried by 0.1-20wt.% on activated carbon obtd. by carbonizing carbonaceous stock, activating the resultant carbon in an atmosphere having  $\leq 15$ vol.% steam content and cooling it to  $\leq 300^{\circ}\text{C}$  in the atmosphere or activated carbon obtd. by treating activated carbon obtd. by the conventional method at  $\geq 500^{\circ}\text{C}$  in gaseous nitrogen and gaseous  $\text{CO}_2$  not contg. oxygen or steam and cooling the treated carbon to  $\leq 300^{\circ}\text{C}$  in the atmosphere. An org. binder is added by 1-50 pts.wt. to 100 pts.wt. of the activated carbon carrying the oxides and they are molded in a honeycomb shape.

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## TECHNICAL FIELD

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[Industrial Application] When this invention is described in more detail, it makes the activated carbon obtained in the specific process support a metallic oxide about the deodorization approach which used a metallic-oxide support activated carbon molding object and this molding object, and it is the honeycomb-like molding object which added and cast the binder, and its oxidation catalyst nature is high and can use it for deodorization of malodorous substances, such as methyl mercaptan and a trimethylamine.

## TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] this invention tend to offer the remover and the removal approaches of an offensive odor , such as the \*\* methyl mercaptan in the deodorization catalyst which consist of a metallic oxide installation activated carbon molding object with high catalyst nature with the low pressure loss which can fully remove gas even if it pass the inside of an oxidation catalyst at high speed and the refrigerator which used it , a toilet , an air cleaner , etc. , and a trimethylamine , in order to remove malodorous substances , such as thin methyl mercaptan and a trimethylamine , in view of the above-mentioned trouble at the low temperature which exist in a life space .

## EFFECT OF THE INVENTION

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[Effect of the Invention] The metallic-oxide support activated carbon molding object of this invention is ordinary temperature or low temperature, and when stinkdamp concentration is very low, it has a function high as an oxidation catalyst, and for the shape of a honeycomb, since pressure loss is very low, it is excellent in the oxidation removal capacity of malodorous substances, such as methyl mercaptan and a trimethylamine. It can use for the remover of stinkdamp, such as methyl mercaptans, such as a refrigerator, a toilet, and an air cleaner, using this property.

## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] When this invention is described in more detail, it makes the activated carbon obtained in the specific process support a metallic oxide about the deodorization approach which used a metallic-oxide support activated carbon molding object and this molding object, and it is the honeycomb-like molding object which added and cast the binder, and its oxidation catalyst nature is high and can use it for deodorization of malodorous substances, such as methyl mercaptan and a trimethylamine.

[0002]

[Description of the Prior Art] Although it is known that a metallic oxide has the catalyst nature which carries out oxidative degradation of the malodorous substances, such as methyl mercaptan and a trimethylamine, when they are used having made the ceramic honeycomb support these, since the specific surface area of a ceramic honeycomb is small, high oxidation activity is not shown. However, high catalytic activity is shown, if

it installs to activated carbon, since there are also few harmful reaction by-products, it is effective as a deodorant, but it cannot be used, if it puts into a small bag or a column is not filled up with the activated carbon of the shape of a grain, or powder. moreover, it is difficult for pressure loss to become high if it is used by such approach, or to pass gas at high speed -- etc. -- there was a trouble.

[0003] Moreover, by the approach of installing a metallic oxide, after preparing conventional honeycomb-like activated carbon, the reinforcement of the honeycomb-like activated carbon used as support was small, since specific surface area was small, it was difficult to make [ many ] the amount of installation of a metallic oxide, and the metallic-oxide support activated carbon of high activity was not obtained.

[0004] For example, when using it as a filter in a refrigerator, a toilet, an air cleaner, etc., it was unsuitable what installed the metallic oxide from the former to a certain granular activated carbon. That is because it is difficult for pressure loss to pass gas highly at high speed in order to use it, filling up a column and a container with activated carbon.

[0005] Therefore, when using it as such an odor removal filter, in order to remove malodorous substances, such as methyl mercaptan and a trimethylamine, it is high performance as an oxidation catalyst, and honeycomb-like metallic-oxide installation activated carbon with low pressure loss was called for.

[0006]

[Problem(s) to be Solved by the Invention] this invention tend to offer the remover and the removal approaches of an offensive odor , such as the \*\* methyl mercaptan in the deodorization catalyst which consist of a metallic oxide installation activated carbon molding object with high catalyst nature with the low pressure loss which can fully remove gas even if it pass the inside of an oxidation catalyst at high speed and the refrigerator which used it , a toilet , an air cleaner , etc. , and a trimethylamine , in order to remove malodorous substances , such as thin methyl mercaptan and a trimethylamine , in view of the above-mentioned trouble at the low temperature which exist in a life space .

[0007]

[Means for Solving the Problem] Prior \*\*\*\*\* publication number, such as this invention person In 7 No. -80299 official report After carbonizing a carbonaceous raw material and carrying out activation in the ambient atmosphere below steam content 15 capacity %, In an ambient atmosphere as it is After processing the activated carbon which cooled to 300 degrees C or less, or was obtained with the conventional method above 500 \*\* in the nitrogen gas which does not contain oxygen or/and a steam substantially, or/and carbon dioxide gas, In the inside of an ambient atmosphere as it is It cools to 300 degrees C or less. Further Iron, chromium, Metallic oxide containing a kind chosen from the group of the metal which consists of nickel, cobalt, manganese, zinc, copper, magnesium, and calcium, or two sorts or more The metallic-oxide installation activated carbon which has the oxidation catalyst nature made to support 0.1 to 20% of the weight Methyl mercaptan, \*\*\*\*\* excellent in the removal engine performance of stinkdamp, such as a trimethylamine.

[0008] Before carrying out activation and fully cooling after activation reaction termination in an ambient atmosphere quite higher than steam content 15 capacity %, "the activated carbon obtained with the conventional method" is taken out from an activation furnace, and means the activated carbon obtained by the usual process contacted to air here. Moreover, "excluding oxygen or/and a steam substantially", in heat

treatment of activated carbon, it is the semantics of an ambient atmosphere in which the oxygen atom combined with the activated carbon front face does not exist, and oxygen and a steam say 1 - 2% or less of condition.

[0009] In order that this invention person etc. might remove malodorous substances, such as thin methyl mercaptan and a trimethylamine, at the low temperature which exists in a life space based on this, pressure loss which can be used in a refrigerator, a toilet, an air cleaner, etc. was low, and he examined many things about the activated carbon which made the metallic oxide excellent in the oxidation catalyst nature of a malodorous substance support. consequently, pass a specific process as support -- if it casts in the shape of [ which the built activated carbon was used / in the shape of / and made the metallic oxide support ] a back honeycomb -- 0-40-degree C low temperature -- 10 ppm also in the low concentration of extent, the oxidation removal of the malodorous substances, such as methyl mercaptan and a trimethylamine, can fully be carried out -- very -- high -- this invention was reached [ that an activity metallic-oxide support activated carbon molding object is acquired and ] based on a header and this.

[0010] A carbonaceous raw material is carbonized. Namely, steam content 15 capacity % (Hereafter, when displaying a gaseous presentation by %, capacity % shows, and it is only displayed as %) After carrying out activation in the following ambient atmospheres, In an ambient atmosphere as it is In the inside of the nitrogen gas which does not contain oxygen or/and a steam for the activated carbon cooled and obtained to 300 degrees C or less, or the activated carbon obtained with the conventional method substantially, or/and carbon dioxide gas After processing above 500 degrees C, In the inside of an ambient atmosphere as it is To the activated carbon cooled and obtained to 300 degrees C or less The oxide of a kind or two sorts or more of metals chosen from the group which consists of iron, chromium, nickel, cobalt, manganese, zinc, copper, magnesium, and calcium 0.1 - 20 % of the weight (hereafter, when displaying the presentation of a solid-state and a liquid by %, weight % shows) It is only displayed as %. Activated carbon made to support They are the metallic-oxide support activated carbon molding object which has the oxidation catalyst nature which adds the organic system binder 1 - 50 weight sections to the 100 weight sections, and it makes it come in the shape of a honeycomb to cast, and the offensive odor deodorization approach characterized by using the molding object.

[0011] This invention is explained in detail below.

[0012] As a carbonaceous raw material, the activated carbon used for this invention carbonizes carbonaceous raw materials, such as coconut \*\*\*\* and coal, and is obtained by carrying out activation by the approach of this invention.

[0013] Under the present circumstances, although activation gas contains others, the choke damp, or/and nitrogen gas, it is necessary to make steam content into 15% or less. [ steam ] Usually, the presentation of the gas for activated carbon activation currently used is 40 - 60% of steams, and is higher than it in many cases. Since the activation rate of the carbonaceous by the steam is more remarkable than the choke damp and quick, the presentation of activation gas is usually set up so that a steam partial pressure may become as high as possible. Therefore, the conditions of this invention are the mild conditions which made the activation rate late remarkably compared with the conventional method. Especially this point is important, and a metallic oxide is installed to the activated carbon by which activation was carried out under the special conditions of this invention so that it may mention later, and the deodorant ability excellent only in

the case of the molding object which added the organic system binder is demonstrated. [0014] As shown in the example 5 and the examples 5 and 6 of a comparison of Table 3, when activation is carried out under the conditions that steam content is high, it is admitted that the oxidation catalyst nature of malodorous substances, such as methyl mercaptan and a trimethylamine, is falling clearly. Although the detail of the device in which the activation conditions that steam content is low raise the oxidation catalyst ability of activated carbon is not clear, it is pointed out that the honeycomb-like activated carbon obtained under such conditions is in the condition that the oxygen atom combined with the front face does not exist. Moreover, micropore smaller than the aperture of the activated carbon obtained with the conventional method is developed, and the honeycomb-like activated carbon obtained under such conditions has structure suitable for support of a metallic oxide.

[0015] Although manufactured by carrying out activation of the carbonaceous raw material cast in the shape of a honeycomb by the steam, combustion gas, etc., even if usual honeycomb-like activated carbon uses such activated carbon for this invention, it does not show sufficient oxidation catalyst engine performance. After supporting a metallic oxide with the gas of the above specific presentations using the activated carbon by which activation was carried out, the effectiveness of this invention adds and extrudes an organic system binder, and will not be acquired without using the activated carbon molding object to which the shape of a honeycomb was given.

[0016] Thus, the obtained honeycomb-like activated carbon shows the high catalyst nature which oxidizes malodorous substances, such as methyl mercaptan and a trimethylamine, promptly. However, the raw material activated carbon of this invention is taken out out of a system with an after [ activation ] elevated temperature, and if it is left in the ambient atmosphere which contains a steam, hydrogen gas, or oxygen gas so much, the capacity as an oxidation catalyst will decline remarkably.

[0017] After activation is the basis of the gas of the same presentation as the time of activation, and the activated carbon of this invention needs to cool below to temperature 300 \*\*, and needs to take out activated carbon out of a system after that. The gas used for activation and the gas used for cooling may not necessarily be the things of the same presentation that the gas of the same presentation as the time of the activation needed at the time of cooling should just be the ambient atmosphere of the nitrogen gas which does not contain oxygen or/and a steam substantially, carbon dioxide gas, or these mixed gas. The ambient atmosphere of the above presentations is pointed out as carrying out "cooling in an ambient atmosphere as it is" in this invention.

[0018] Activated carbon after activation If it takes out in air above 300 degrees C, the capacity as a low-temperature low-concentration oxidation catalyst will decline remarkably. The effect affect the catalyst nature the case where it cools in after [ activation ] nitrogen gas, and at the time of cooling in air is shown in the example 1 and the example 1 (what was cooled in air by the after [ activation ] conventional method) of a comparison of Table 1. Moreover, the effect the temperature with which after [ activation ] activated carbon touches air affects catalyst nature is shown in the example 4 and the examples 3 and 4 of a comparison of Table 2.

[0019] The specific surface area of the activated carbon of this invention which is the above, and was made and obtained is 800m<sup>2</sup>/g. It is desirable that it is above, and it is more desirable if it is more than 1000m<sup>2</sup>/g.

[0020] Furthermore, it is temperature in the above-mentioned activation gas and the gas of the same presentation about the spent carbon with which air etc. was touched, the front face oxidized in this invention, and oxidation catalyst nature fell, or the activated carbon obtained by the conventional method. It processes above 500 degrees C and cools below to temperature 300 \*\* in the gas. Thus, the metallic-oxide support activated carbon molding object in which high oxidation catalyst nature is shown is acquired to malodorous substances, such as methyl mercaptan and a trimethylamine, by making a metal oxide catalyst support the obtained activated carbon as mentioned above as a raw material, and adding and casting an organic system binder further. If it puts in another way, high oxidation catalyst nature will be given to honeycomb-like activated carbon by such heat treatment and cooling. The activated carbon with which this heat treatment is applied could be obtained from what kind of raw materials, such as coal and coconut \*\*\*\*, and especially the configuration before heat treatment is not limited.

[0021] By carrying out the above-mentioned processing also to the activated carbon prepared by the usual approach, activated carbon support usable as an oxidation catalyst of this invention is obtained. Under the present circumstances, processing temperature It may be necessary to be 500 degrees C or more. Although the processing time changes with temperature, in 500 \*\*, it is usually 20-180. A part is desirable and the effectiveness is enough acquired by processing for several minutes in 800 \*\*. The effect heat treatment temperature affects oxidation catalyst nature is shown in the examples 2 and 3 and the example 1 of a comparison of Table 1.

[0022] Although obtained by whether activation of the activated carbon of this invention is carried out on conditions [ \*\*\*\* ], or it heat-treats on conditions [ \*\*\*\* ], not only the difference in the engine performance of activated carbon but the interaction of the surface structure of activated carbon etc. and an organic system binder is considered by the reason which shows the deodorant ability excellent in the activated carbon molding object of this invention. That is, it is required for an organic system binder not to check the adsorption engine performance of activated carbon.

[0023] In the activated carbon support used by this invention, it is a metallic oxide. It is necessary to make it support 0.1 to 20%. for making activated carbon support a metallic oxide -- a water solution -- or -- if it requires -- acid concentration the liquid end after having dissolved the metal salt of the specified quantity in the acid water solution of 0.1 to 3 convention, having been immersed, stirring activated carbon in this solution and making a metallic oxide adsorb enough -- carrying out -- inside of air or nitrogen It dries below 300 degrees C. Or the water solution of a metal salt, for example, water solutions, such as a cupric chloride, may be prepared by the approach of back-drying sprinkled over homogeneity, stirring activated carbon by a mixer etc. Heat treatment decomposes and the metal salt installed by support serves as a metallic oxide. Although it is necessary to make the amount of support of a metallic oxide into 0.1 - 20%, the case where the amount of support is 0.5 - 5% is more desirable.

[0024] The amount of support of a metallic oxide Since catalyst nature will not improve comparatively with many amounts of support and the adsorption engine performance of the activated carbon itself which is support will be checked if catalytic activity is inadequate and it becomes 20% or more when it is 0.1% or less, it is necessary to make the amount of installation into 20% or less. Accommodation of the amount of support of a metallic oxide is performed by changing the ratio of the amount of the metallic oxide in



a water solution or an acid water solution, and the amount of activated carbon. Usually, the metallic oxide in a solution is adsorbed by activated carbon nearly completely.

[0025] If organic-acid salts, such as inorganic-acid salts, such as a nitrate, a sulfate, and a carbonate, and acetate, an oxalate, formate, or a hydroxide, a chloride, etc. are usable and it is changed into an oxide by subsequent heat treatment as a metal salt, it can use widely. Moreover, the mixture of these salts is also usable. Furthermore, it can also be used in the state of the water solution which added acids, such as a hydrochloric acid, a nitric acid, a sulfuric acid, an acetic acid, and formic acid, as an acid of the counter ion of a salt.

[0026] It is necessary to make the activated carbon support of this invention support the oxide of a kind or two sorts or more of metals chosen from the group which consists of iron, chromium, nickel, cobalt, manganese, zinc, copper, magnesium, and calcium. When the number of the metallic oxides made to support one, or two kinds may be made to mix and support and two or more metallic oxides are used together, its catalyst engine performance may improve further.

[0027] It is not necessary to use as a metallic oxide completely the metal salt supported not necessarily, and in order to change the metal salt which activated carbon was made to support to a metallic oxide, heat treatment is required, but even if non-decomposed salts remain, when the metallic oxide is contained, it has the function as an oxidation catalyst. Heat treatment is usually in air or nitrogen. It is carried out at the temperature of 300 degrees C or less. Thus, the metallic-oxide installation activated carbon of this invention is obtained.

#### [Embodiment of the Invention]

[0028] thus, particle diameter ground when requiring in order to cast the obtained metallic-oxide installation activated carbon in the shape of a honeycomb 0.1 micrometers - 4mm about -- the metallic-oxide support activated carbon of various particle size is usable, and it can be used according to the purpose of use, being able to choose.

[0029] The organic system binder used by this invention is a binder which consists of quality of organic, and when it mixes with activated carbon powder and pressurizes under humid, it hardly needs to check adsorbent [ of activated carbon ] while it forms molding. The drainage system binder in which plasticity is shown is desirable, for example, the following moisture powder system binders, a water-soluble binder, etc. are usable.

[0030] As a moisture powder system binder, a butadiene copolymer latex, an isoprene copolymer latex, a vinyl-acetate-resin emulsion, an acrylic emulsion, a polyolefine system emulsion, and microorganism production polysaccharide [the product made from Takeda Chemical Industries ] P-1, for example, "BIOPORI" etc., are mentioned.

[0031] As a water-soluble binder, cellulotics, such as methyl cellulose, a carboxymethyl cellulose, ethyl cellulose, and hydroxypropylcellulose, polyvinyl alcohol, a polyvinyl butyral, a polyethylene glycol, etc. are mentioned.

[0032] Generally it extrudes and various functions quality of organic, such as a binder, a dispersant, a wetting agent, lubricant, a plasticizer, and a water retention agent, is used together by molding in many cases. Therefore, these organic system binder is not only used independently, but is added as mixture containing two or more quality of organic in many cases.

[0033] Moreover, lubricant and a wetting agent may be mixed if needed. As these additives, ceramic powder, such as a wax emulsion, a stearic acid emulsion, a glycerol, alcohol, vinyl acetate resin, polyethylene, polypropylene, and also a bentonite, etc. is

mentioned. The commercial item beforehand blended as these molding assistants may be used as it is.

[0034] The amount of the organic system binder used is activated carbon. It is necessary to consider as the one to 50 section to the 100 sections. It is the two to 25 section preferably. It is because the front face of activated carbon is covered with an organic system binder, so adsorbent and catalyst nature will fall if the 1 or less section of the reinforcement of a molding object is [ the amount of the organic system binder used ] insufficient and the amount of the organic system binder used becomes the 50 or more sections. The effect the amount of the organic system binder used affects the reinforcement and catalyst nature of a molding object is shown in the examples 14-17 of Table 6, and the examples 9-12 of a comparison.

[0035] A well-known approach can be used for casting in the shape of a honeycomb. That is, as mixed approaches, such as activated carbon and a binder, a mixer, a ribbon mixer, a static mixer, a ball mill, a sample mill, a kneader, etc. can be used, for example. By adding and kneading the water solution of an initial complement in the case of mixing, it is made the shape of rice cake, and it can extrude and can cast by a vacuum extrusion briquetting machine etc. Moreover, in the case of mixing, after adding water to a binder and fully mixing, the approach of mixing activated carbon is also effective. It is the need of being cautious of the appearance into which mixing to homogeneity enough and air bubbles do not go. Moreover, it is necessary to carry out a vacuum deairing and degassing enough with a vacuum extruder.

[0036] The grid-like dice of a square shape is attached and it is made for circular to the mouthpiece of an extruder or the extruded molding to become honeycomb-like. Especially the magnitude of a dice is not limited but the thing of the range usually used is used. Moreover, although there is especially no limit also about the number of cels, it is 50-800 from a viewpoint of moldability. Cel extent is desirable. In addition, the number of cels means the number of the holes generally included in a 1 square inch.

[0037] Although the honeycomb-like molding object extruded and acquired is usually dried in air or nitrogen after it is cut into suitable die length, it is cautious of the appearance by which a crack does not go into the wall surface of a honeycomb at the time of desiccation. It dries at the temperature of 300 degrees C or less. The metallic-oxide support activated carbon molding object of this invention is acquired by this.

[0038] The metallic-oxide support activated carbon molding object of this invention has very low pressure loss because of a honeycomb-like molding object, and it is ordinary temperature or low temperature, and since it has a function high as an oxidation catalyst also when the concentration of stinkdamp, such as methyl mercaptan, is very low, it excels as a remover of stinkdamp, such as a refrigerator, a toilet, and an air cleaner.

[0039]

[Example] Hereafter, an example is given and this invention is explained still more concretely.

[0040] (Examples 1-17, examples 1-12 of a comparison) An example 1 Propane combustion gas after distilling dryly the coconut husks pulverized to 10-30 meshes by 800 \*\* (gas presentation; 80% of nitrogen) After carrying out activation using oxygen 0.2 %, carbon-dioxide-gas 9.8 %, and 10% of steams until it was set to specific-surface-area of 1300m<sup>2</sup>/g by 900 \*\*, activated carbon was taken out in the container which carried out the nitrogen purge, it cooled below to 300 \*\* in nitrogen gas, and activated

carbon support was obtained.

[0041] Next, neglect cooling was taken out and carried out into air, and the example 1 of a comparison obtained activated carbon support, after cooling until it took out in nitrogen the activated carbon which carried out activation until specific surface area was set to 1300m<sup>2</sup>/g like the example 1, and it became 500 \*\*. Furthermore, after processing the activated carbon support of the example 1 of a comparison for 10 minutes by 500 \*\* in nitrogen, it took out in nitrogen, it cooled to the room temperature, and the activated carbon support of an example 2 was obtained. Moreover, after processing the activated carbon support of the example 1 of a comparison for 5 minutes by 800 \*\* in 50% of nitrogen, and the air current of 50% of carbon dioxide gas, it cooled to the room temperature in nitrogen, and the activated carbon support of an example 3 was obtained.

[0042] The metallic oxide which shows these activated carbon in Tables 1-6 as follows was made to support. It is the amount of metallic-oxide support as an example. The case where 2.0% of metallic-oxide support activated carbon is prepared is shown. After adding 50g of activated carbon support, stirring, after dissolving the amount which contains 1g for a necessary metal salt as a metal in pure water, and leaving it for 12 hours, a ridge is carried out and it dries at 60 degrees C, and it is the amount of metallic-oxide support. 2.0% of metallic-oxide support activated carbon was obtained.

[0043] In addition, when making the metallic oxide of two or more components support, it was carrying out by having repeated the above-mentioned actuation, and prepared. Moreover, the class of metallic oxide and a series of support activated carbon with which the amounts of support differ were also prepared according to the above-mentioned approach.

[0044] Thus, the obtained metallic-oxide support activated carbon was ground to 0.01 - 0.1 mm. This support activated carbon 100 The extrusion molding binder 20 section [the YUKEN INDUSTRY CO., LTD. make and a water-soluble extrusion molding binder "SERANDA YB115IW"] was often mixed in the section, the pure-water 30 section was added to it, and it often kneaded by the kneader. Extrusion molding binder ("SERANDA YB115IW") It is the binder which has blended all of a binder, a plasticizer, lubricant, a wetting agent, etc. with sufficient balance, and can cast only by adding water.

[0045] The presentation of a binder consists of an organic system compound with little ash content, and is excellent in heat-resistant resolvability. After carrying out homogeneity mixing of support activated carbon and the organic system binder, it extruded and cast by the vacuum extruder. The configuration of knockout molding is 300 at 50mm angle. It was a cel.

[0046] It cut by the thickness of 10mm, it dried by 150 \*\*, and the sample which carried out knockout molding prepared the metallic-oxide support activated carbon molding object. The prepared honeycomb molding object has sufficient reinforcement, and generating of fines etc. was not seen.

[0047] In addition, in the example 2 of a comparison, the commercial honeycomb-like ceramic manganese catalyst ["manganese CHIDDO" By Kobe Steel] was used.

[0048] The deodorant ability trial was performed by the following approach common to all examples and examples of a comparison. It is methyl mercaptan 409mg as an offensive odor component. Or the trimethylamine was used, when it was left on certain conditions for 24 hours, the continuation flow test was performed, and the degree of a fall of stinkdamp concentration was measured.

[0049] Methyl mercaptan 409mg after it sets one prepared various honeycomb molding object catalysts in a 4l. desiccator and they carry out a vacuum deairing Or after pouring in trimethylamine 24mg, the open air was introduced, and it returned to ordinary pressure, and was left at 5 degrees C for 24 hours. The amount of the poured-in stinkdamp was equivalent to the amount of stinkdamp for five years generated in the refrigerator of average ordinary homes, and was followed as the guide of a deodorization trial. That is, the initial load for five years was given to one honeycomb molding object catalyst. Next, this catalyst is set to the reactor made from an acrylic with a diameter [ of 10cm ], and a die length of 30cm, and it is methyl mercaptan or trimethylamine 3ppm. The included air was circulated at 5 degrees C. The rate of flow was set to SV=31200 hr-1, and relative humidity was made into 50\*\*10%. Outlet gas was sampled by the syringe and concentration was analyzed by gas chromatography.

[0050] A measurement result and the used description of a catalyst are shown in Table 1.

[0051]

[Table 1]

	試料触媒	比表面積 m <sup>2</sup> /g	冷却ガス	触媒 ( )内は添着量 wt%	初期負荷24時間 後のメチルメルカプタン 残存量/ppm	メチルメルカプタン出口濃度/ppm				
						30分	60分	90分	120分	180分
実施例1	活性炭ハニカム	1060	N <sub>2</sub>	Mn(2.0) + Cu(1.0)	0.1	ND	ND	ND	ND	ND
比較例1	活性炭ハニカム	1030	空気	Mn(2.0) + Cu(1.0)	26	0.8	1.0	1.2	1.4	1.6
比較例2	市販ゼミックスハニカム触媒	—	—	Mn(2.0)	38	2.2	2.6	2.8	2.7	2.8
実施例2	比較例1を500℃N <sub>2</sub> 中処理	1030	N <sub>2</sub>	Mn(2.0) + Cu(1.0)	1.0	ND	ND	0.1	0.1	0.1
実施例3	比較例1を800℃N <sub>2</sub> +CO <sub>2</sub> 中処理	1030	N <sub>2</sub>	Mn(2.0) + Cu(1.0)	0.5	ND	ND	ND	0.1	0.1

[0052] Each honeycomb-like metallic-oxide support activated carbon molding object (examples 1-3) of this invention removed nearly completely the methyl mercaptan which is a malodorous substance, and showed the outstanding deodorization capacity. As shown in the example of a comparison (1 2) on the other hand, when the activated carbon support obtained with conventional methods other than this invention or a commercial catalyst was used, the removal rate of methyl mercaptan was all slow.

[0053] Next, when taking out the activated carbon which carried out activation like the example 1, made the activated carbon into which the temperature when taking out after cooling and in air in N<sub>2</sub> was changed, and the metallic oxide was made to support with the same approach as an example 1, and the metallic-oxide support activated carbon molding object cast in the shape of a honeycomb was acquired. By the same approach as an example 1, the removal engine performance of trimethylamine gas was measured using these activated carbon molding objects.

[0054] The description of the activated carbon molding object used is shown in Table 2. in addition, the trimethylamine concentration in the air which the initial load of a trimethylamine is 24mg and was used for the continuation flow test -- 3 ppm it is .

[0055]

[Table 2]

	取り出し 温度 ℃	比表面積 m <sup>2</sup> /g	( ) 触媒 内は添着量 wt%	初期負荷24時間 後のトリメチルアミン 残存量/ppm	トリメチルアミン出口濃度/ppm				
					30分	60分	90分	120分	180分
実施例 4	300	1060	Mn(2.0) + Cu(3.0)	0.3	0.1	0.1	0.2	0.1	0.2
比較例 3	350	1000	Mn(2.0) + Cu(3.0)	3.8	0.3	0.5	0.6	0.7	0.8
比較例 4	400	1020	Mn(2.0) + Cu(3.0)	5.4	0.4	0.4	0.5	0.6	0.8

[0056] As shown in Table 2, depending on the temperature to which the engine performance of the honeycomb-like metallic-oxide support activated carbon of this invention contacts air for the first time after cooling, it turns out above 300 \*\* that the removal capacity of stinkdamp declines sharply.

[0057] Next, it sets on the conditions from which the steam partial pressure of activation gas differs in case activation of the coconut shell charcoal is carried out. After carrying out activation until it is set to specific-surface-area of 1200m<sup>2</sup>/g by 900 \*\*, activated carbon is taken out in the container permuted with nitrogen. Cooled below to 300 \*\* in this nitrogen, the metallic oxide was made to support with the still more nearly same approach as an example 1, the metallic-oxide support activated carbon molding object cast in the shape of a honeycomb was used, and the removal engine performance of trimethylamine gas was measured by the same approach as an example 1.

[0058] The description of the activated carbon molding object used is shown in Table 3. in addition, the trimethylamine concentration in the gas which the initial load of a trimethylamine is 24mg and was used for the continuation flow test -- 3 ppm it is .

[0059]

[Table 3]

	比表面積 m <sup>2</sup> /g	賦活ガス H <sub>2</sub> O:CO <sub>2</sub> :N <sub>2</sub> :O <sub>2</sub>	冷却 ガス	( ) 触媒 内は添着量 wt%	初期負荷24時間 後のトリメチルアミン 残存量/ppm	トリメチルアミン出口濃度/ppm				
						30分	60分	90分	120分	180分
実施例 5	1060	14:25:60.9:0.1	N <sub>2</sub>	Mn(2.0) + Cu(3.0)	0.3	0.1	0.1	0.2	0.1	0.2
比較例 5	1040	17:22:60.8:0.2	N <sub>2</sub>	Mn(2.0) + Cu(3.0)	1.6	0.3	0.3	0.4	0.5	0.7
比較例 6	1050	20:19:60.9:0.1	N <sub>2</sub>	Mn(2.0) + Cu(3.0)	2.3	0.3	0.5	0.6	0.8	0.9

[0060] If the engine performance of the honeycomb-like metallic-oxide support activated carbon of this invention shows high catalyst nature and steam concentration rises and puts it in another way depending on the steam concentration at the time of activation when steam concentration is 15% or less as shown in Table 3, as for the activated carbon obtained on the conditions that an activation rate is high, it will be admitted that oxidation catalyst nature falls quickly.

[0061] Next, the support activated carbon into which the metallic oxide made to support with the same approach as an example 1 was changed was prepared, it extruded like the example 1, it cast and the activated carbon molding object was prepared. Moreover, the activated carbon molding object which does not make a metallic oxide support for a comparison was prepared. These activated carbon molding objects were used and methyl mercaptan and the removal engine performance of trimethylamine gas were measured by the same approach as an example 1.

[0062] The description of the activated carbon molding object used is shown in Tables 4 and 5. In addition, initial load of methyl mercaptan It is 409mg and the initial load of methyl mercaptan is 24mg. moreover, the methyl mercaptan in the gas used for the

continuation flow test or the concentration of a trimethylamine -- 3 ppm it is .

[0063]

[Table 4]

	( ) 触媒 内は添着量 wt%	初期負荷24時間 後のメチルメルカプタン 残存量/ppm	メチルメルカプタン出口濃度/ppm				
			30分	60分	90分	120分	180分
実施例 6	Mn(2.5)	0.2	ND	ND	ND	0.1	0.1
実施例 7	Mn(2.0) + Ca(1.5)	0.3	ND	ND	ND	0.1	0.1
実施例 8	Cu(3.0) + Ni(1.0)	0.5	0.1	0.1	0.1	0.2	0.2
実施例 9	Cu(2.0) + Zn(2.0)	0.8	ND	0.1	0.1	0.2	0.1
比較例 7	—	12.4	1.4	1.5	1.7	2.0	2.2

[0064]

[Table 5]

	( ) 触媒 内は添着量 wt%	初期負荷24時間 後のトリメチルアミン 残存量/ppm	トリメチルアミン出口濃度/ppm				
			30分	60分	90分	120分	180分
実施例10	Ni(1.0) + Cu(5.0)	0.2	0.1	0.2	0.1	0.1	0.2
実施例11	Cr(2.5) + Cu(4.0)	0.3	0.2	0.1	0.1	0.2	0.2
実施例12	Co(2.0) + Fe(3.0)	0.3	0.1	0.2	0.2	0.2	0.2
実施例13	Mg(1.5) + Fe(3.5)	0.2	0.1	0.1	0.2	0.2	0.2
比較例 8	—	8.5	2.0	1.9	2.1	2.4	2.3

[0065] As shown in Tables 4 and 5, it is honeycomb-like metallic-oxide support activated carbon (examples 6-13) of this invention. Although the oxidation catalyst engine performance of stinkdamp, such as methyl mercaptan and a trimethylamine, was excellent, it was admitted that the activated carbon molding object (examples 7 and 8 of a comparison) which is not supporting the metal salt had the low removal engine performance.

[0066] Furthermore, the trial which changed the addition of the organic binder used at the time of extrusion molding was performed. The metallic-oxide support activated carbon powder prepared like the example 1 was extruded [ changed the addition of an organic binder, kneaded it and ] and cast. As an organic binder, it cast using the binder (examples 16 and 17 and examples 11 and 12 of a comparison) which mixed the carboxymethyl-cellulose (CMC) 2 section and the bentonite 15 section in "above-mentioned SERANDA YB115IW" (examples 14 and 15 and examples 9 and 10 of a comparison) and the microorganism production polysaccharide molding assistant "BIOPORI P-1" [product made from Takeda Chemical Industries ] 83 above-mentioned section.

[0067] The removal performance test of methyl mercaptan gas was performed like the example 1 using those activated carbon molding objects. in addition, initial load of methyl mercaptan the concentration of the methyl mercaptan in the air which is 409mg and was used for the continuation flow test -- 3 ppm it is . Moreover, the collapse strength test (the direction of a b-axis) of a molding object was performed.

[0068] The result is shown in Table 6. Here, BP is CMC about BIOPORI. BT shows a bentonite for a carboxymethyl cellulose again.

[0069]

[Table 6]

	有機バインダー量 g/部	有機バインダー種類	圧縮強度 kg/cm <sup>2</sup>	比表面積 m <sup>2</sup> /g	脱離 ( ) 内は蒸着量 wt%	初期負荷24時間 後の残存量/ppm	メチルメルカプタン出口濃度/ppm				
							30分	60分	90分	120分	180分
比較例9	0.5	セラランダー	1.6	1090	Mn(2.0) + Cu(1.0)	0.2	ND	ND	0.1	0.1	0.1
実施例14	5.0	セラランダー	34.5	1080	Mn(2.0) + Cu(1.0)	0.1	ND	ND	ND	ND	ND
実施例15	20.0	セラランダー	41.8	1060	Mn(2.0) + Cu(1.0)	0.1	ND	ND	ND	ND	ND
比較例10	55.0	セラランダー	55.2	760	Mn(2.0) + Cu(1.0)	4.2	0.3	0.3	0.6	1.3	1.7
比較例11	0.5	BP+CMC+BT	2.4	1120	Mn(2.0) + Cu(1.0)	0.2	ND	ND	ND	0.1	0.1
実施例16	10.0	BP+CMC+BT	36.8	1090	Mn(2.0) + Cu(1.0)	0.3	ND	0.1	0.1	0.2	0.2
実施例17	25.0	BP+CMC+BT	44.9	1040	Mn(2.0) + Cu(1.0)	0.4	ND	0.1	0.2	0.2	0.2
比較例12	60.0	BP+CMC+BT	52.7	740	Mn(2.0) + Cu(1.0)	3.9	0.2	0.4	0.7	1.0	1.4

[0070] When the addition of an organic binder is the one to 50 section, as shown in Table 6 The stinkdamp removal engine performance, collapse reinforcement -- being large (examples 14-17) -- case (examples 9 and 11 of a comparison) where the addition of a binder is the 1 or less section When the reinforcement of a honeycomb-like molding object fell, and practical use was not borne and a binder is used the 50 or more sections (examples 10 and 12 of a comparison) The fall of a methyl mercaptan malodorous substance removal rate was large. Moreover, fines had generated neither of the cases on the honeycomb molding object.

[0071]

[Effect of the Invention] The metallic-oxide support activated carbon molding object of this invention is ordinary temperature or low temperature, and when stinkdamp concentration is very low, it has a function high as an oxidation catalyst, and for the shape of a honeycomb, since pressure loss is very low, it is excellent in the oxidation removal capacity of malodorous substances, such as methyl mercaptan and a trimethylamine. It can use for the remover of stinkdamp, such as methyl mercaptans, such as a refrigerator, a toilet, and an air cleaner, using this property.

## CLAIMS

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### [Claim(s)]

[Claim 1] After carbonizing a carbonaceous raw material and carrying out activation in the ambient atmosphere below steam content 15 capacity %, In an ambient atmosphere as it is To the activated carbon cooled and generated to 300 degrees C or less The oxide of a kind or two sorts or more of metals chosen from the group which consists of iron, chromium, nickel, cobalt, manganese, zinc, copper, magnesium, and calcium Activated carbon 100 which made 0.1 - 20 % of the weight support Metallic-oxide support activated carbon molding object which has the oxidation catalyst nature which adds the organic system binder 1 - 50 weight sections to the weight section, and it makes it come to cast in the shape of a honeycomb.

[Claim 2] It is temperature in the nitrogen gas which does not contain oxygen or/and a steam for the activated carbon obtained with the conventional method substantially, or/and carbon dioxide gas. After processing above 500 degrees C, To the activated carbon cooled and generated below to 300 \*\* in the ambient atmosphere as it is The oxide of a kind or two sorts or more of metals chosen from the group which consists of iron, chromium, nickel, cobalt, manganese, zinc, copper, magnesium, and calcium Activated carbon which made 0.1 - 20 % of the weight support Metallic-oxide support activated carbon molding object which has the oxidation catalyst nature which adds the organic system binder 1 - 50 weight sections to the 100 weight sections, and it makes it come to cast in the shape of a honeycomb.

[Claim 3] In the ambient atmosphere as it is after carbonizing a carbonaceous raw material and carrying out activation in the ambient atmosphere below steam content 15 capacity % Activated carbon cooled and obtained to 300 degrees C or less The activated carbon obtained with the conventional method or in the nitrogen gas which does not contain oxygen or/and a steam substantially, or/and carbon dioxide gas In the ambient atmosphere as it is after processing above temperature abbreviation 500 \*\* To the activated carbon cooled and obtained to 300 degrees C or less The oxide of a kind or two sorts or more of metals chosen from the group which consists of iron, chromium, nickel, cobalt, manganese, zinc, copper, magnesium, and calcium Activated carbon which made 0.1 - 20 % of the weight support The deodorization approach characterized by using the metallic-oxide support activated carbon molding object which added the organic system binder 1 - 50 weight sections to the 100 weight sections, and was cast in the shape of a honeycomb, and which has oxidation catalyst nature.